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(54) Title: PROCEDURE FOR TREATING CELLULOSE DERIVATIVE FIBRES

(57) Abstract

The present invention concerns improving the properties of cellulose carbamate fibres. The wet strength properties in particular can be improved by treating the fibres with alkalis or organic bases, aiming to reduce the number of carbamate groups. The procedure may also be applied in the manufacturing of regenerated cellulose fibres.

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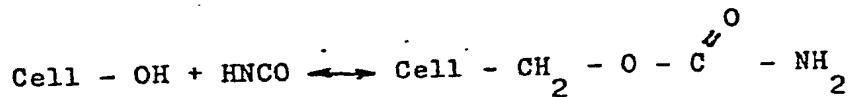
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Procedure for treating cellulose derivative fibres

The present invention concerns a procedure for treating cellulose derivative fibres. More specifically, the invention concerns a procedure for regulating the properties of cellulose carbamate fibres. Furthermore, the invention concerns a novel procedure for 5 manufacturing regenerated cellulose fibres.

In the Finnish patent application Nos. 793226 and 810226 is disclosed a procedure for manufacturing an alkali-soluble cellulose derivative from cellulose and urea at elevated temperature. The 10 procedure is based on the fact that on heating urea to its melting point or to a higher temperature it begins to decompose into isocyanic acid and ammonia. Isocyanic acid in itself is not a particularly stable compound: it tends to trimerize into isocyanuric acid. Furthermore, isocyanic acid also tends to react with urea, 15 whereby biuret is formed. Isocyanic acid also reacts with cellulose, producing an alkali-soluble cellulose derivative which is called cellulose carbamate. The reaction may be written as follows:-

20



25 The cellulose compound thus produced, cellulose carbamate, may be dried subsequent to washing and stored even over prolonged periods, or it may be dissolved in an aqueous alkali solution for manufacturing fibres, for instance. From this solution can be manufactured cellulose carbamate fibres or films by spinning or by extruding, in 30 like manner as in the viscose manufacturing process. The keeping quality of cellulose carbamate and its transportability in dry state afford a great advantage compared with cellulose xanthate in the viscose process, which cannot be stored nor transported, not even in solution form.



If, for instance, continuous fibre or filament manufactured from cellulose carbamate appropriate for textile uses is desired, the carbamate is first dissolved in alkali, e.g. in aqueous sodium hydroxide solution. From this solution may then be precipitated 5 fibre or film, for instance in like manner as in the manufacturing of viscose fibre cellulose is regenerated from the NaOH solution of cellulose xanthate. In this connection, the cellulose carbamate solution is spun through spinnerets into an acid precipitation bath, which causes precipitation of the cellulose carbamate. The 10 precipitation may also be accomplished into lower alcohols such as methanol, ethanol or butanol, or into hot aqueous salt solutions.

The properties of precipitated fibres are substantially influenced by the nitrogen content of the fibre, that is, the number of carbamate groups in the cellulose chain. It has been found that the 15 carbamate groups increase the sensitivity of the fibres to water and, simultaneously, they impair the wet properties of the fibres. In some cases, this is even an advantage, whereas in other cases it is detrimental because, for instance in textile uses, the fibres 20 are most often expected to have good wet strength.

The object of the present invention is a procedure by which the properties of cellulose carbamate fibres, in particular their wet 25 properties, can be regulated as desired so that fibres suitable for each purpose are obtained. The procedure according to the invention for regulating the properties of cellulose carbamate fibres is characterized in that the fibres are treated with alkali or with an organic base.

30 By the aid of an alkali treatment according to the invention, the carbamate groups of the cellulose carbamate can be removed to the desired degree. Thus for instance the wet strength of the fibres substantially increases, while the wet strechability decreases. If, again, for instance fibres for non-woven purposes are desired 35 which have good water absorption capacity and swelling capacity, the alkali treatment of the invention may be carried out in a milder form.



It is possible to carry the alkali treatment of cellulose carbamate fibres so far that a near complete removal of the carbamate groups from the fibres takes place. A fibre has then been obtained of which the solubility in alkali has gone down to the same level as that of regenerated cellulose fibres obtained by the viscose method, that is, less than 10%. In fact, a regenerated cellulose fibre is concerned, manufactured if a different way from the regenerated cellulose fibre of the viscose method. Thus, an object of the invention is a new process for manufacturing regenerated cellulose fibres comprising the treatment of cellulose carbamate fibres with an alkali or an organic base for substantially removing the carbamate group from the fibres. In a broader sense, by the invention is provided a new process for manufacturing regenerated cellulose fibres, this process being characterized by the following steps: dissolving cellulose carbamate in alkali, spinning or precipitating the carbamate solution to cellulose carbamate fibres or filaments, and conversion of the cellulose carbamate fibres or filaments to regenerated cellulose by treating the fibres with alkali or with an organic base. In the different steps of the process any procedures or means may be used which result in accomplishment of said method steps, and as examples may be mentioned the procedures disclosed in the Finnish Patents No. 61033 and 62318 and Finnish patent applications No. 814208 and 814209.

Towards regulating the properties of cellulose carbamate fibres as taught by the invention, any alkali or organic base may be used. Sodium hydroxide and potassium hydroxide are suitable alkalis, and among organic bases may be mentioned as examples tetramethylammonium hydroxide and ethylene diamine. The amount of alkali or base required depends on the alkali used in each case. When using sodium hydroxide, the concentration of the alkali solution is preferably less than 2%, because larger NaOH quantities may adversely affect the properties of the fibre. The suitable NaOH quantity is in the range 0.1 to 2%. Potassium hydroxide does not act as powerfully as sodium hydroxide, and when it is used the suitable quantity is in the range of 0.1 to 4%. Organic bases are not as powerful as the above-mentioned, and therefore, the concentration range appropriate



in their case may vary in the range of 0.1 to 10%.

The treatment time and temperature depend greatly on how large a proportion of the carbamate groups one desires to eliminate. For 5 instance, a treatment at room temperature may be applied, although in that case the required treatment times may become quite long. The treatment times can be shortened by raising the temperature, even down to a few minutes. A temperature suitable in practice is mostly from room temperature to 100°C, but higher temperatures may 10 be used if treatment means capable of containing pressure are at disposal.

The invention is described more in detail in the embodiment examples included. The percentages stated in the examples are to be understood as per cent by weight. The wet strengths of staple 15 fibres mentioned in the examples were determined by procedures which are readable in: BISFA (International Bureau for the Standardization of Man-Made Fibers), Internationally agreed method for testing regenerated cellulose and acetate staple fibres, 1970 Edition. The fibres were air-conditioned at 23°C and 50% relative 20 humidity.

Example 1

Cellulose carbamate fibres were manufactured as follows. Bleached 25 spruce sulphate cellulose (400 g) with DP brought to the level of 390 by the aid of γ radiation was impregnated at -40°C with 3.3 litres of liquid ammonia in which had been dissolved 400 g urea. The cellulose was kept in this solution below the boiling point of ammonia for six hours, whereafter it was taken into room temperature. On evaporation of the ammonia, the urea cellulose was placed 30 in a vacuum oven at 135°C for three hours. An air flow produced by a water jet pump passed through the oven all the time.

The reaction product was washed with methanol, three times with 35 water and once with methanol. The air-dry product had DP 340 and nitrogen content 1.7%. A solution was prepared by dissolving the

cellulose carbamate thus manufactured in 10% NaOH solution, containing also ZnO for better solubility. The carbamate content of the solution was 5.5% and the ball viscosity, 50 seconds. Of the solution was determined the clogging number by the procedure presented in: H. Sihtola, Paperi ja Puu 44 (1962), No. 5, p. 295-300. The clogging number of the solution was found to be 495. The solution was pressed into sulphuric acid solution through a spinneret with 100 holes having diameter 0.09 mm. The precipitating solution contained 10% sulphuric acid, 7% aluminium sulphate and 20% sodium sulphate.

In connection with precipitation, the fibres were stretched 0-80% to improve their strength properties. Subsequent to washing and drying, cellulose carbamate fibres A-G were obtained which were used in the other examples. In Table I are presented the manufacturing conditions of the fibres.

TABLE I

FIBRE	DISSOLVING		PRECIPITATION Stretching (%)
	NaOH (%)	ZnO (%)	
A	10	1,0	0
B	10	1,0	50
C	10	1,0	75
D	10	1,0	80
E	10	1,5	0
F	10	1,5	50
G	10	1,5	75

Example 2

35 Fibres manufactured as in Example 1 were treated with NaOH solutions having various concentrations. The wet properties of the fibres were determined before and after the alkali treatment. The



alkali solubility of the fibres was determined using the standard method SCAN - C2:61 and 5.5% NaOH solution.

5 In Table II following below are presented the properties of the fibres and after the NaOH treatment. The table reveals that alkali treatment of cellulose carbamate fibres improves the fibres' wet strength properties if the alkali concentration is at a reasonable level. When the alkali concentration goes up to 21%, the strength properties of the fibres deteriorate. When the alkali 10 treatment is carried out at elevated temperature, better strength properties are achieved with considerably shorter treatment times. Stretching the fibres at the spinning phase also has a beneficial effect on the strength properties.

15 Example 3

As in Example 2, NaOH treatments of cellulose carbamate fibres were carried out using elevated temperatures. Table III gives the properties of the fibres before and after the alkali treatment. The 20 table reveals that remarkably short treatment times are achieved using the temperature 100°C.

Example 4

25 As in Example 2, alkali treatments of cellulose carbamate fibres were carried out. Potassium hydroxide was used for alkali. Table IV presents the properties of the fibres before and after the alkali treatment.

30 The results reveal that potassium hydroxide is not quite as efficient as sodium hydroxide. Higher alkali concentrations than in the case of NaOH may be used in the treatment.

Example 5

35 As in Example 2, alkali treatments of cellulose carbamate fibres were carried out. Tetramethylammonium hydroxide was used as alkali.



Table V presents the properties of the fibres before and after the alkali treatment.

Example 6

5 Fibres manufactured as in Example 1 were treated with NaOH so that
a substantial part of the carbamate groups were removed and the
alkali solubility of the fibres was lowered to the level of regen-
erated fibres obtained in the viscose process. In Table VI are
10 presented the properties of the fibres before the alkali treatment
and the properties of the regenerated fibres after the alkali
treatment.



TABLE I I

FIBRE CHARACTERISTICS BEFORE
ALKALI TREATMENT

Fibre	ALKALI TREATMENT				FIBRE CHARACTERISTICS AFTER ALKALI TREATMENT								
	Alkali solubil. %	Nitrogen content %	Wet strength cN/dtex	Distens. when wet %	Modulus. when wet cN/dtex	Alkali conc. %	Temper- ature °C	Time h	Alkali solubil. %	Nitrogen content %	Wet strength cN/dtex	Distens. when wet %	Modulus. when wet cN/dtex
A	86,3	1,1	0,8	53	3	0,5	23	70	75,0	0,3	0,8	17	8
C	86,9	"	0,9	10	13	0,5	"	"	52,9	0,3	1,4	10	14
"	"	"	"	"	"	2,0	"	"	6,7	0,2	0,9	9	9
D	86,8	1,0	1,1	15	14	0,25	40	5	77,1	0,8	1,3	13	14
"	"	"	"	"	"	0,50	"	"	62,3	0,5	1,2	10	15
"	"	"	"	"	"	0,75	"	"	44,8	0,5	1,4	11	16

TABLE III

Fibre	FIBRE CHARACTERISTICS BEFORE ALKALI TREATMENT				FIBRE CHARACTERISTICS AFTER ALKALI TREATMENT				FIBRE CHARACTERISTICS AFTER ALKALI TREATMENT					
	Alkali solubil.	Nitrogen content	Wet strength	cN/dtex	Modulus when wet	Alkali conc.	Temperature °C	Time h	Alkali conc.	Nitrogen content	Wet strength	cN/dtex	Modulus cN/dtex	Time h
E	86,0	1,1	0,7	73	2	0,5	60	24	21,2	0,2	0,8	43	3	
F	"	"	0,9	30	7	"	"	"	18,7	"	1,2	13	12	
G	"	"	1,0	10	11	"	"	"	17,0	0,3	1,5	10	16	
D	86,8	1,0	1,1	15	14	"	100	0,05	19,1	0,4	1,5	12	15	
"	"	"	"	"	"	"	"	0,2	8,5	0,1	1,5	9	19	



TABLE IV

FIBRE CHARACTERISTICS BEFORE
ALKALI TREATMENTFIBRE CHARACTERISTICS AFTER
ALKALI TREATMENT

Fibre	Fibre characteristics before alkali treatment			Fibre characteristics after alkali treatment			Modulus when wet cN/dtex	Dilatn. when wet %	Wet strength cN/dtex	Nitrogen content %	Alkali conc. %	Temperature °C	Time h
	Alkali solubil. %	Nitrogen content %	Wet strength cN/dtex	Alkali solubil. %	Nitrogen content %	Wet strength cN/dtex							
B	88,0	1,1	0,8	32	7	0,5	22	72	77,6	0,6	1,0	1,9	10
"	"	"	"	"	"	1,0	"	"	59,5	0,5	1,0	1,8	9
"	"	"	"	"	"	2,0	"	"	29,5	0,4	1,1	1,5	10
"	"	"	"	"	"	0,5	100	0,2	38,5	0,3	1,1	1,2	11
F	"	"	0,9	30	"	"	"	"	1,0	12,1	0,2	1,2	12
"	"	"	"	"	"	"	"	"	0,2	22,0	0,3	1,1	11
"	"	"	"	"	"	"	"	"	1,0	7,3	0,2	1,2	11

TABLE V

Fibre	FIBRE CHARACTERISTICS BEFORE ALKALI TREATMENT				ALKALI TREATMENT				FIBRE CHARACTERISTICS AFTER ALKALI TREATMENT				
	Alkali solubl.	Nitrogen content	Wet strength	Distens. when wet cN/dtex	Modulus when wet cN/dtex	Alkali conc.	Temper- ature °C	Time h	Alkali conc.	Nitrogen content	Wet strength	Distens. when wet cN/dtex	
	χ	χ	χ	χ	χ	χ	χ	χ	χ	χ	χ	χ	
F	88,0	1,1	0,9	30	7	0,5	22	72	88,0	0,6	1,0	21	6
"	"	"	"	"	"	1,0	"	"	74,6	0,5	1,0	18	7
"	"	"	"	"	"	2,0	"	"	67,0	0,3	1,0	18	7
"	"	"	"	"	"	0,5	100	0,2	50,0	0,3	1,0	18	9
"	"	"	"	"	"	2,0	"	"	0,5	16,8	0	1,2	13
"	"	"	"	"	"	"	"	"	1,0	-11,7	0,1	1,0	11
"	"	"	"	"	"	"	"	"	"	"	"	11	11

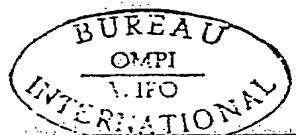


TABLE VI

Fibre	FIBRE CHARACTERISTICS BEFORE ALKALI TREATMENT				ALKALI TREATMENT				FIBRE CHARACTERISTICS AFTER ALKALI TREATMENT				
	Alkali solubil.	Nitrogen content	Wet strength cN/dtex	Distens. %	Modulus cN/dtex	Alkali conc.	Temper- ature °C	Time h	Alkali conc. %	Time h	Nitrogen content	Wet strength cN/dtex	Distens. %
A	86,3	1,1	0,8	53	3	2,0	23	70	1,1	0,1	0,7	17	8
D	86,8	1,0	1,1	15	14	0,5	100	0,25	6,1	0	1,6	10	15
"	"	"	"	"	"	"	"	1,0	1,8	0	1,4	8	17

Claims

1. Procedure for regulating the wet properties of cellulose carbamate fibres, characterized in that the fibres are treated with alkali or with an organic base.

5 2. Procedure according to claim 1, characterized in that cellulose carbamate fibres are treated with aqueous NaOH or KOH solution.

3. Procedure according to claim 2, characterized in that the fibres are treated with 0.1-2% NaOH or KOH solution.

10 4. Procedure according to claim 1, characterized in that carbamate fibres are treated with 0.1-10% tetramethylammonium hydroxide or with ethylene diamine.

15 5. Procedure according to any one of claims 1 to 4, characterized in that the treatment is carried out at elevated temperature.

6. Procedure towards manufacturing regenerated cellulose fibres, characterized in that cellulose carbamate fibres are treated with alkali or with an organic base for substantially totally removing 20 the carbamate groups.

7. Procedure for manufacturing regenerated cellulose fibres, characterized in that the procedure comprises the following steps:-
25 (a) dissolving cellulose carbamate in alkaline conditions,
(b) spinning or precipitating the cellulose carbamate solution to cellulose carbamate fibres or filaments, and
(c) treating cellulose carbamate fibres or filaments with alkali or with an organic base for removing the carbamate groups and obtaining 30 regenerated cellulose fibres or filaments.



INTERNATIONAL SEARCH REPORT

International Application No. PCT/FI83/00028

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ¹

According to International Patent Classification (IPC) or to both National Classification and IPC ² 3

D 01 F 11/02, D 01 F 2/00, C 08 B 15/06

II. FIELDS SEARCHED

Minimum Documentation Searched ⁴

Classification System	Classification Symbols
IPC 3 US Cl	C 08 B 15/06, 16/00, D 01 F 2/00, 2/02, 2/24, 11/00, 11/02 536:30, 56, 57

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched ⁵

SE, NO, DK, FI classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴

Category ⁶	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
A	FI, B, 61 033 (NESTE OY) 29 January 1982	
A, P	EP, A2, A3, 57 105 (NESTE OY) 4 August 1982	

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IV. CERTIFICATION

Date of the Actual Completion of the International Search ¹⁹

1983-06-23

Date of Mailing of this International Search Report ²⁰

1983-07-06

International Searching Authority ²¹

Swedish Patent Office

Signature of Authorized Officer ²²

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